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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D21C 11/00, 11/04, B01D 43/00, B01F 7/00, 7/04, G05D 7/00, 9/00 — A1

(11) International Publication Number: WO 97/42372

(43) International Publication Date: 13 November 1997 (13.11.97)

(21) International Application Number: PCT/US97/05591

(22) International Filing Date: 3 April 1997 (03.04.97)

(30) Priority Data:
08/642,496 3 May 1996 (03.05.96) US

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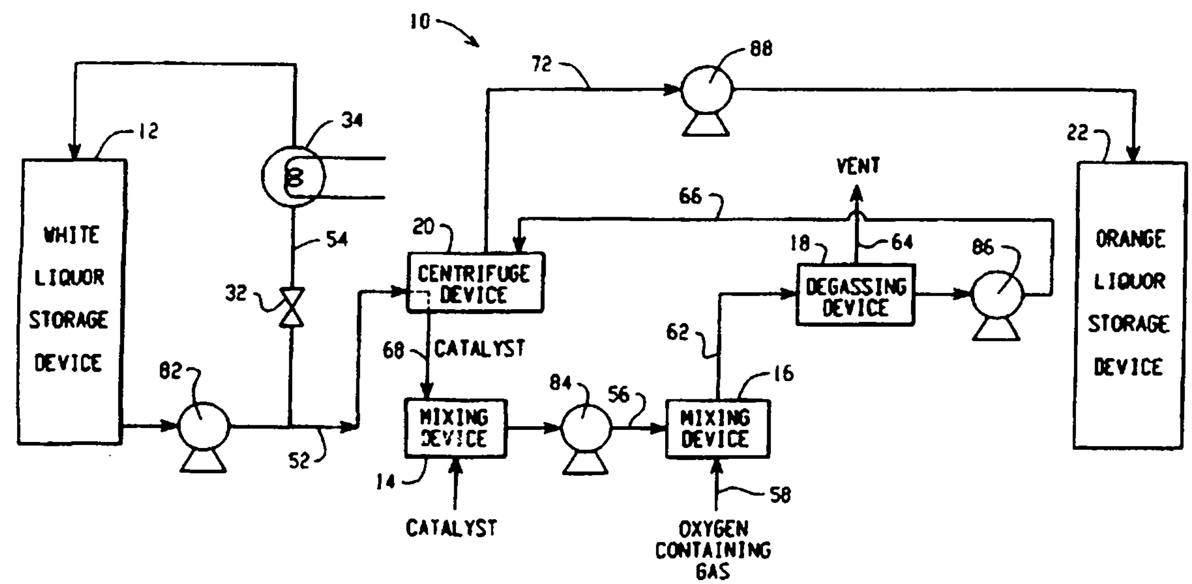
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD AND APPARATUS FOR MAKING POLYSULFIDES BY OXIDIZING SULFIDES



(57) Abstract

A process and system for making polysulfides or orange liquor for use in the paper pulping industry are disclosed. The process comprises the steps of forming a slurry comprised of a white liquor and a catalyst or catalysts, introducing an oxygen-containing gas into the slurry, mixing the slurry and said oxygen-containing gas under pressure to form a polysulfide-containing slurry, degassing the polysulfide-containing slurry to form a degassed slurry and extracting polysulfides, or orange liquor, from the polysulfide-containing slurry. The system comprises a pressurized mixer (16), a degassing liquid/level control device (18) and a centrifuge (20).

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METHOD AND APPARATUS FOR MAKING POLYSULFIDES BY OXIDIZING SULFIDES

Field of the Invention

The present invention relates generally to a process and a system for making polysulfides for use in the paper pulping industry, and more particularly, to a process and a system for producing polysulfides conventionally referred to as "orange liquor" in the paper pulping industry.

Background of the Invention

In some paper pulping processes, a polysulfide commonly referred to as "orange liquor" is utilized. Orange liquor is typically produced by mixing a catalyst(s) and an oxidizing agent with a sulfide-containing pulp liquor conventionally referred to as "white liquor."

The present invention provides a process and a system for increasing the rate of production and the yield of polysulfides over processes known heretofore.

Summary of the Invention

In accordance with the present invention, there is provided a process for making polysulfides comprising the steps of: forming a slurry comprised of a white liquor and a catalyst, introducing an oxygen-containing gas to the slurry, mixing the slurry and the oxygen-containing gas under pressure to form a polysulfide-containing slurry, degassing the polysulfide-containing slurry to form a degassed slurry and separating the polysulfide, i.e., orange liquor, from catalysts and returning the reclaimed catalysts to the incoming white liquor.

It is an object of this invention to provide a process for producing polysulfides for use in the pulping of wood to produce paper.

It is a further object of this invention to provide a system for producing polysulfides for use in the pulping of wood to produce paper.

It is a further object of the present invention to provide a process as described above that increases the rate of production and the yield of polysulfides over processes known in the art.

It is a further object of the present invention to increase the yield of polysulfides by 10% to 15% over the present state of the art.

It is a further object of the present invention to provide a process as described above that mixes and

oxidizes white liquor, under pressure, with air, pure oxygen or an admixture of both, in the presence of a catalyst.

It is a further object of this invention to provide a degassing chamber that facilitates the separation of a gas from a liquid and also maintains the proper liquid level in a mixer.

It is a further object of the present invention to provide a process, as described above, that mixes the white liquor catalyst and oxygen-containing agent.

It is a further object of the present invention to run a reaction that oxidizes sulfide to polysulfides at a temperature of from about 50 degrees Celsius to about 100 degrees Celsius, preferably from about 60 degrees Celsius to about 90 degrees Celsius and, most preferably, at about 80 degrees Celsius.

It is a further object of the present invention to provide a system for producing orange liquor, comprising: a pressurized mixer having an inlet to receive a slurry comprising white liquor and a catalyst; a degassing liquid/level control device; means for conveying a slurry comprising orange liquor and said catalyst from said pressurized mixer to said degassing liquid/level control device; a centrifuge device; and, means for conveying said slurry comprising said orange liquor and said catalyst from said degassing liquid/level control device

to said centrifuge device.

These and other objects will become apparent from the following description of a preferred embodiment taken together with the accompanying drawing.

Brief Description of the Drawing

The invention may take physical form in certain parts and arrangement of parts, a preferred embodiment of which will be described in detail in the specification and illustrated in the accompanying drawing which form a part hereof, and wherein:

Fig. 1 is a schematic representation of a system for producing a method of forming polysulfides according to the present invention.

Detailed Description of a Preferred Embodiment

Referring now to the drawing wherein the purpose is the showing of a preferred embodiment of the present invention only and not for the purpose of limiting the same, Fig. 1 schematically illustrates system 10 for producing polysulfides illustrating a preferred embodiment of the present invention.

Broadly stated, system 10 includes a storage device 12, a mixing device 14, a mixing device 16, a degassing/liquid level control device 18, a centrifuge device 20, and a storage tank 22. More specifically, storage device 12 is a storage tank that contains a white liquor, and specifically the sulfides to be oxidized to

polysulfides. Mixing device 14 is a conventionally known mixing device typically used in the art (e.g., a trough with a screw type mixer). A feed line 52 (i.e., piping) connects storage device 12 to a solids purge chamber in the centrifuge device 20. A feed line 68 carries the white liquor and catalysts to mixing device 14. A pump device 82 is provided to convey white liquor through feed line 52 to centrifuge device 20. Feed line 52 includes a return line 54 to white liquor storage device 12. Return line 54 includes a flow-control valve 32 and a heating element 34.

A feed line 56 connects mixing device 14 with mixing device 16. A pump device 84 is provided in feed line 56 to convey material from mixing device 14 to mixing device 16.

Mixing device 16 is provided to mix fluid material in liquid and gaseous forms. According to one aspect of the present invention, mixing device 16 is adapted to mix components under pressure. More specifically, a mixing device 16 is provided for mixing the white liquor and a catalyst, or catalysts, with an oxygen containing gas under a pressure greater than atmospheric pressure, as will be described in greater detail below. These mixers are generally known in the art; however, according to the present invention, these mixers must be capable of maintaining a positive pressure of reactive gas therein.

A mixing device which finds advantageous application with the present invention is disclosed in copending U.S. Patent Application Serial Number 08/382,213, entitled A CONTINUOUS DYNAMIC MIXING SYSTEM AND METHODS FOR OPERATING SUCH SYSTEM, filed January 30, 1995, which disclosure in incorporated herein by reference.

A gas feed line 58 is connected at one end to a source (not shown) of oxygen-containing gas and at the other end to mixing device 16 to supply oxygen-containing gas thereto.

Line 62 connects mixing device 16 to degassing device 18. Degassing device 18 is a conventionally known component for removing gas from liquid material. To this end, a vent line 64 extends from degassing device 18.

A line 66 connects degassing device 18 to centrifuge device 20. A pump 86, preferably a gear pump, is provided in feed line 66 to facilitate transfer of material from degassing device 18 to centrifuge device 20. Centrifuge device 20 is also a conventionally known device used for separating components forming a material. In the embodiment shown, centrifuge device 20 may be a decanter type of a disk type centrifuge.

A first feed line 68 connects centrifuge device 20 to mixing device 14 to re-circulate material to mixing device 14, as will be described in greater detail below. A second feed line 72 connects centrifuge device 20 to

storage device 22. A pump 88 is provided in feed line 72 to facilitate transfer of material from centrifuge device 20 to storage device 22.

System 10, as heretofore described, is provided to facilitate a process for making polysulfides, or orange liquor, for use in the pulping of wood. As will be appreciated, the sizes and capacities of the respective components are matched to accommodate each other. In one embodiment, as shown in Fig. 1, the sulfide values in a paper pulping liquor, particularly a white liquor, may be continuously oxidized to polysulfides by employing air or another oxidizing gas, as the oxidizing medium, in the presence of a catalytic metal compound(s).

Referring now to the operation of system 10, white liquor in its liquid state, is stored in storage device 12. Preferably, the temperature of the white liquor is maintained at 50 to 100 degrees Celsius. To maintain the temperature of the white liquor in storage device 12, it may be re-circulated through feed line 54, wherein heating element 34 is utilized to provide heat to control and maintain the desired temperature. The white liquor in storage device 12 is pumped by pump 82 through line 52 into mixing device 14. Mixing device 14 is where the white liquor is mixed with a catalyst, the catalyst being metal oxides such as manganese oxides, manganese dioxide and other metal oxide catalysts known in the art. The

mixing trough mixes the white liquor with the catalyst or catalysts into a homogeneous slurry. The metal catalyst, i.e., the manganese oxide, manganese dioxide, cerium oxide, alumina or mixtures thereof, is blended in mixing device 14 with the white liquor to form a slurry. The concentration of metal catalyst is preferably from about 1 to about 20% by weight of white liquor. More preferably, the concentration of catalyst to liquor is greater than 5% by weight. Manganese dioxide is a preferred metal catalyst, and the use of manganese dioxide particles having a particle size of less than 45 microns is preferable. More preferable is the use of a catalyst as disclosed in copending U.S. patent application serial number 08/565,087, entitled NOVEL CATALYST FOR THE OXIDATION OF SULFIDES, filed on November 30, 1995, which disclosure is incorporated herein by reference.

The catalysts/white liquor slurry in mixing device 14 is then conveyed to a mixing device 16 by pump 54 through line 56.

A continuous stream of an oxygen-containing gas is introduced into mixing device 16 from a gas supply through feed line 58. The use of air is preferable; however, any gas containing oxygen in sufficient quantities to react with the white liquor may be used as long as the other constituents of the gas do not react

with the slurry. It is to be noted than an over abundance of oxygen is not detrimental to the production of polysulfides. Importantly, the slurry and the oxygen-containing gas present within mixing device 16 is maintained at a pressure greater than atmospheric pressure. Operationally, the pressure within mixing device 16 may be as high as or equal to 300 psig.

In a pilot plant configuration, a flow of air into mixing device 16 at a rate of about 1 cubic foot per minute to about 20 cubic feet per minute is desirable, with a flow rate of air of about 8 cubic feet per minute preferable. A flow of 8 cubic feet per minute results in a pressure within mixing device 16 of about 95 psig.

As indicated above, having more oxygen than the stoichiometric amount is not problematic and, in fact, may be desirable. Air to oxygen mixtures ranging from air to pure oxygen may be used. Mixtures by volume from about 1 to 1 to about 4 to 3 of air to oxygen are preferable in the case where a mixture of air and oxygen is used.

The white liquor converts to orange liquor within an operating temperature range of from about 50 degrees Celsius to about 100 degrees Celsius. Preferably, the operating temperature ranges from about 60 degrees Celsius to about 90 degrees Celsius, and most preferably is about 80 degrees Celsius.

Mixing device 16, in a pilot plant configuration, mixes the catalyst containing slurry at an agitator tip speed of about 1 to about 100 ft/s. The higher tip speed promotes better gas/liquid/catalysts mixing resulting in higher conversion of sodium sulfide in the white liquor to polysulfide. The most preferable tip speed is an optimization of conversion efficiency and power requirements for the mixing device.

Complete mixing of the white liquor with catalyst is accomplished after about 10 seconds to about 20 minutes, more preferably after about 2 minutes to about 5 minutes.

Inasmuch as mixing device 16 operates at a pressure higher than atmospheric pressure, mixing device 16 must be capable of operating and sustaining pressures greater than atmospheric pressure and less than the apparent, operational upper limit of about 300 psig.

Under pilot plant conditions, the residence time of the slurry in mixing device 16 is from about 10 seconds to about 10 minutes, with a preferable residence time of about 1 minute. It has been discovered that as the tip speed of the agitator increases, a higher concentration of polysulfides is produced independent of the mixing time.

The polysulfides containing slurry produced in mixing device 16 is conveyed to a degassing/liquid level control device 18. The purpose of the device 18 is to

remove the oxygen-containing gas from the polysulfide-containing slurry and to maintain the proper slurry level in mixing device 16. The liquid level in device 18 is maintained to ensure a flooding condition within mixing device 16.

It is believed that the chemical reaction that converts the sulfides to polysulfides continues in device 18. The reaction tapers off as the gas elutes from the polysulfide-containing slurry and escapes to the atmosphere through vent 64.

The pressure in degassing device 18 may run from about 1 psig to about 300 psig. As the gas elutes from the polysulfide-containing slurry, little foam is produced. If the vent gas contains a significant amount of unreacted oxygen - as could be the case if oxygen enriched air or pure oxygen is used - it can be repressurized and added to the oxygen containing gas, through line 58, entering mixing device 16.

Mixing device 16 and the degassing device 18 are approximately equal volume. The residence time of the polysulfide-containing slurry in both mixing device 16 and degassing device 18 is about 15 seconds to about 10 minutes, and preferably about 1 minute to about 2 minutes.

After degassing, a degassed slurry is pumped by pump 86 through line 66 to a centrifuge device 20. The

purpose of the centrifuge device is to separate the orange liquor from the catalysts. Centrifuge devices as typically known in the industry may be used. However, a decanter or disk type of centrifuge is preferable.

Basically, the degassed slurry enters the centrifuge device 20 and orange liquor exits via one route, i.e., line 72, and the catalyst is flushed with white liquor entering centrifuge device 20 from line 52 and exits via a different route, i.e., line 68. The catalyst stream in line 68 may have a catalyst concentration that is typically about 1 to 30 percent and preferably about 5 to 10 percent.

The catalyst stream may be sent through feed line 68 back to the mixing device 14 to be used again in the process of oxidizing sulfides to polysulfides. In the process of this invention, the catalyst particles are typically used more than once.

Importantly, the g force of centrifuge device 20 must be set so as to effect a removal of catalysts from orange liquor but not effect the removal of other solids normally present in white liquor. Typical g forces produced by centrifuge device 20 may range from about 500 g to about 3,000 g. The g forces are preferably from about 1,000 g to about 2,000 g.

The orange liquor that has been separated from the degassed slurry is pumped by pump 88 through feed line 72

to storage device 22. Polysulfide concentrations of about 8 grams per liter have been realized through the use of the process disclosed herein.

Use of the process disclosed herein may result in an increase of the yield of polysulfides of from about 10% to about 15% over yields known heretofore.

The following is an example illustrating the production of polysulfides from sulfides on a pilot plant scale.

EXAMPLE

The production of a polysulfide cooking liquor containing about 7.37 g/L and 7.52 g/L (expressed as Na_2O) using the system described herein is described.

In this example, the mixing device used is the same as disclosed in copending U.S. patent application serial number 08/382,213.

White liquor containing 31.0 g/L Na_2S (expressed as Na_2O) is pumped from the white liquor storage tank device to the mixing device 14 at a temperature of 90 degrees C via a gear pump 82. In mixing device 14, the white liquor is mixed with spent manganese oxide catalyst from the centrifuge device 20 to form a slurry that is about 7.3% by weight catalyst. The slurry is pumped to the mixing device 16 via a gear pump 84. The flow rate to the mixing device is controlled by a level controller on the degassing device 18, which is mounted after the

mixing device. The controller adjusts the rotational speed of feed pump 84 that provides the slurry to mixing device 16 to maintain a contact level in the degassing device 18.

The mixing device 16 is maintained at 95 psig air pressure, and accepts an air flow of 8 cubic feet per minute. The mixing device 16 is driven by a 10 H.P., 1,750 rpm motor. Within mixing device 16, air is dispersed via porous metal frits and intense agitation. This is the primary reaction chamber where oxygen is absorbed from the air into the slurry. The absorbed oxygen subsequently oxidizes the spent catalyst, which in turn reacts with white liquor, to form orange liquor. The flow through mixing device 16 is about 0.75 gallons per minute, which allows for about a 2 minute residence time for the slurry.

The resulting slurry is discharged into degassing device 18 at 95 psig to remove suspended air bubbles. The degassing device level is monitored by a controller which adjusts the rotational speed of feed pump 84 that provides mixing device 16 with the catalyst containing slurry. The control of feed pump 84 ·ubsequently controls the flow rate to mixing device 16 and degassing device 18. The slurry is discharged to the centrifuge device 20 at 0.75 gpm.

The centrifuge device 20 is operated at atmospheric

pressure. The bowl rotates at 4,830 rpm, which provides for a g-force of 2,319 x g. The internal scroll rotates at 4,224 rpm. The slurry is separated into solids, i.e., catalyst(s), discharge and orange liquor discharge. The solids, i.e., catalyst(s) are dropped into the mixing device 14 at a rate of about 0.5 lb. per minute. The orange liquor is fed to a storage tank device 22 at a rate of about 0.75 gpm and a temperature of about 82 degrees C.

These and other aspects of the present invention will be appreciated upon the reading and understanding of the specification.

What is claimed is:

1. A process for making polysulfides, comprising the steps of:

(A) forming a slurry comprised of a white liquor and a catalyst;

(B) introducing an oxygen-containing gas to said slurry;

(C) mixing said slurry and said oxygen-containing gas in a mixer under pressure to form a polysulfide-containing slurry;

(D) degassing with a degasser said polysulfide-containing slurry to form a degassed slurry; and

(E) separating said polysulfides from said polysulfide containing slurry.

2. The process of claim 1, wherein said catalyst that remains after step (E) is recycled to said white liquor of step (A).

3. The process of claim 1, wherein said degasser maintains a flooded level of said polysulfide-containing slurry in said mixer.

4. The process of claim 1, wherein said oxygen containing gas, comprises a mixture of oxygen and air with the

concentration of air ranging from 0% up to about 100%.

5. The process of claim 1, wherein said oxygen containing gas is air.

6. The process of claim 1, wherein said mixer has a mixing blade with a tip, the speed of said tip ranging from about 1 to about 100 ft/s.

7. The process of claim 6, wherein said tip speed is about 50 ft/s.

8. The process of claim 1, wherein said pressure ranges from about 1 to about 300 psig.

9. The process of claim 1, wherein said pressure is about 35 psig.

10. The process of claim 1, wherein said polysulfides are extracted from said polysulfide containing slurry by a centrifuge.

11. The process of claim 1, wherein said centrifuge operates with a g force of about 500 to about 3,000.

12. The process of claim 10, wherein said centrifuge

operates with a g force of about 1,800.

13. The process of claim 1, wherein said polysulfide containing slurry is formed with a reaction time of from about 15 seconds to about 10 minutes.

14. The process of claim 1, wherein said polysulfide containing slurry is formed with a reaction time of about 1 minute to about 2 minutes.

15. The process of claim 1, wherein said catalyst is selected from the group consisting of oxides of manganese oxides of cerium, alumina and mixtures thereof.

16. The process of claim 1, wherein said mixer comprises: a mixing chamber having a cylindrical inner wall wherein said inner wall comprises elongated baffles coaxially extending along the major portion of the length of said inner wall, said baffles having a uniform cross-sectional shape corresponding generally to a small geometric segment of a circle, the radius of which is substantially the same as that of the inner wall of said chamber, with the rounded, substantially cylindrical surface of each baffle fitted against the inner wall of said chamber and correspondingly, the flat sides of said baffles facing inwardly;

porous inserts for introducing gas into said mixing chamber wherein said porous inserts are attached to said inwardly facing flat side of said baffles;

a plurality of inlet and outlet means for introducing gaseous materials into said mixing chamber; and,

a multibladed agitator having generally rectangular shaped blades, each of which is rigidly mounted at equally spaced positions on a common hub member which is concentrically rotatable within said mixing chamber by a suitable drive shaft engaging therewith, the dimensions of said blades being suitable to effect axial and radial mixing within said mixing chamber while reducing shear stresses within said fluid material.

17. The process of claim 15, wherein about 68% of the total weight of said catalyst has a particle size of about 45 microns or smaller.

18. The process of claim 17, wherein said catalyst has a concentration of about 1% to about 20% by weight in said slurry.

19. The process of claim 1, wherein the mixing under step (C) is controlled to maintain a temperature of said slurry from about 50 degrees Celsius to about 100 degrees Celsius.

20. The process of claim 1, wherein the mixing under step (C) is controlled to maintain a temperature of said slurry of about 80 degrees Celsius.

21. The process of claim 1, wherein said centrifuge is a decanter or disk type.

22. A system for producing orange liquor, comprising:
(A) a pressurized mixer having an inlet to receive a slurry comprising white liquor and a catalyst;
(B) a degassing liquid/level control device;
(C) means for conveying a slurry comprising orange liquor and said catalyst from said pressurized mixer to said degassing liquid/level control device;
(C) a centrifuge device; and,
(D) means for conveying said slurry comprising said orange liquor and said catalyst from said degassing liquid/level control device to said centrifuge device.

23. The system of claim 22, wherein said pressurized mixer comprises: a mixing chamber having a cylindrical inner wall wherein said inner wall comprises elongated baffles coaxially extending along the major portion of the length of said inner wall, said baffles having a uniform cross-sectional shape corresponding generally to a small geometric segment of a circle, the radius of

which is substantially the same as that of the inner wall of said chamber, with the rounded, substantially cylindrical surface of each baffle fitted against the inner wall of said chamber and correspondingly, the flat sides of said baffles facing inwardly;

porous inserts for introducing gas into said mixing chamber wherein said porous inserts are attached to said inwardly facing flat side of said baffles;

a plurality of inlet and outlet means for introducing gaseous materials into said mixing chamber; and,

a multibladed agitator having generally rectangular shaped blades, each of which is rigidly mounted at equally spaced positions on a common hub member which is concentrically rotatable within said mixing chamber by a suitable drive shaft engaging therewith, the dimensions of said blades being suitable to effect axial and radial mixing within said mixing chamber while reducing shear stresses within said fluid material.

24. The system of claim 22, wherein said pressurized mixer has a mixing blade with a tip, the speed of said tip ranging from about 1 to about 100 ft/s.

25. The system of claim 24, wherein said tip speed is about 50 ft/s.

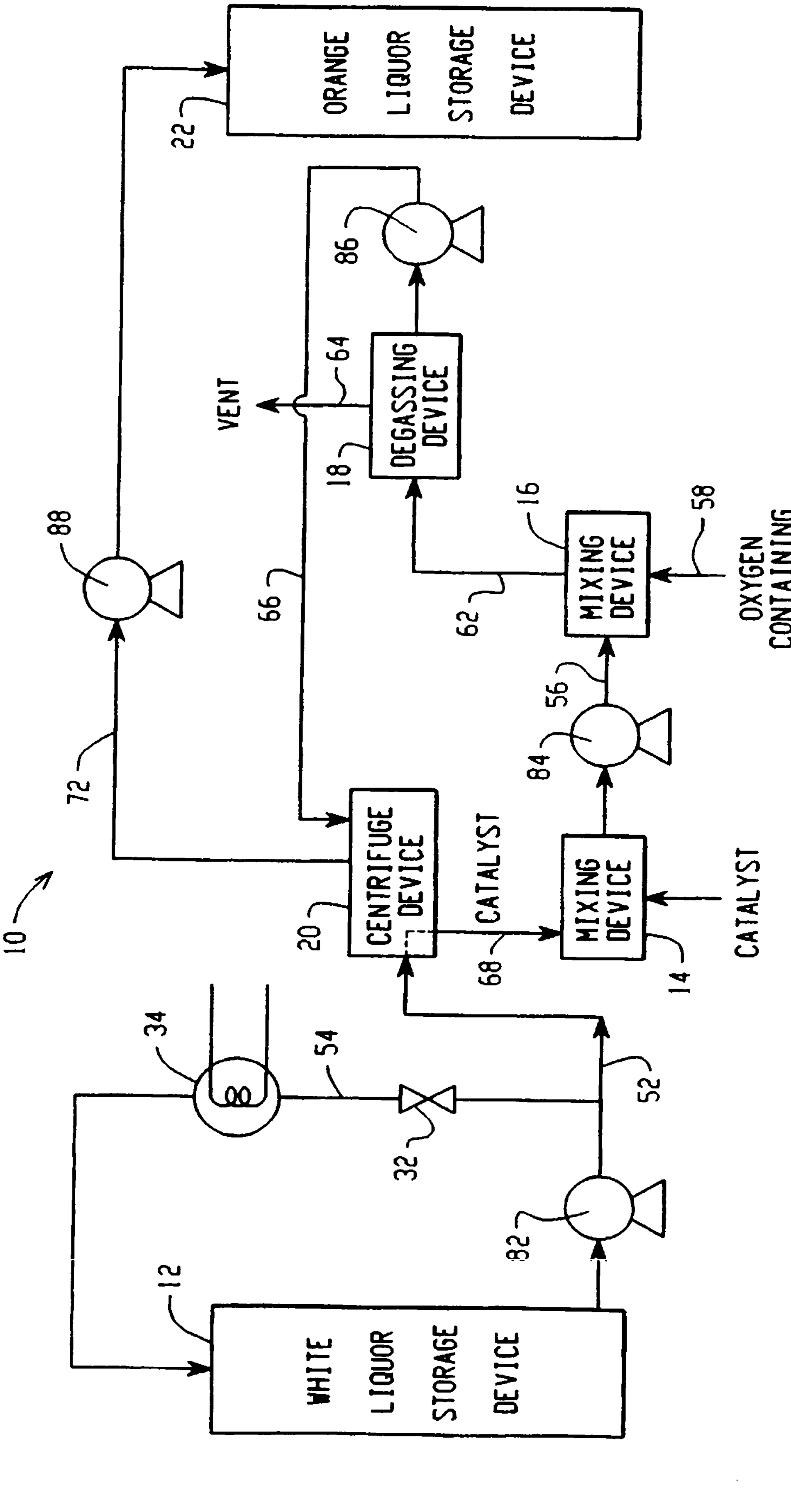
26. The system of claim 22, wherein said pressurized mixer is under a pressure of from about 1 to about 300 psig.

27. The system of claim 26, wherein said pressure is about 35 psig.

28. The system of claim 22, wherein said centrifuge is a decanter or disk type.

29. The system of claim 22, wherein said centrifuge operates with a g force of from about 500 to about 3,000.

30. The system of claim 22, wherein said centrifuge operates with a g force of about 1,800.



ORANGE LIQUOR STORAGE DEVICE
22
86
64
VENT
DEGASSING DEVICE
18
16
58
MIXING DEVICE
OXYGEN CONTAINING GAS
88
66
62
56
84
72
CENTRIFUGE DEVICE
20
CATALYST
MIXING DEVICE
CATALYST
10
68
14
34
54
32
52
82
12
WHITE LIQUOR STORAGE DEVICE

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05591

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :D21C 11/00, 11/04; B01D 43/00; B01F 7/00, 7/04; G05D 7/00, 9/00
US CL :162/30.11, 65, 79; 422/106, 110, 185, 226, 255; 366/102, 168
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/30.11, 65, 79; 422/106, 110, 185, 226, 255; 366/102, 168

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,860,479 A (BARKER et al) 14 January 1975, see entire document.	1-30
Y	US 4,855,123 A (SUZUKI et al) 08 August 1989, see entire document.	1-30
Y	PERRY. R.H. Chemical Engineers' Handbook. 1973. 5th Edition. pages 19.3-19.5.	1-30

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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23 JUNE 1997	22 JUL 1997

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